

## CHEM 221.3, Section 02, Term 2, 2004-5

### Graded Problem Assignment #2: Solutions

**Question 1.** The result (x) of the calculation below is to be input into further calculations. What value should be used?

$$x = (112.37 - 35.23)/(1.046 \times 10^{-2}) - (8.62 \times 10^2)$$

- (a) 6512.8    **(b) 6512.8**    (c) 6513    (d) 651<sub>3</sub>    (e) none of (a), (b), (c) or (d)

**Solution:** product of first subtraction is about 77, and has 2 dp  $\Rightarrow$  4 sf; product of division therefore also has 4sf, and is about 7500  $\Rightarrow$  no decimal places; the last number being subtracted also has no decimal places (862), so the final answer should be rounded to no decimal places. Since the answer is to be input into further calculations, a guard digit is also retained.

Calculator gives 6512.7609.... $\Rightarrow$  6512.8.

**Question 2.** The following data contains a possible outlier. What value of  $Q_{\text{calc}}$  is used in the Q test?

51.3, 53.5, 50.9, 52.0, 51.4, 51.1, 51.7

- (a) 0.73<sub>3</sub>    (b) 0.71<sub>4</sub>    **(c) 0.57<sub>7</sub>**    (d) 0.40<sub>4</sub>    (e) none of (a), (b), (c) or (d)

**Solution:** By inspection, the possible outlier is 53.5.  $Q = \text{gap}/\text{range} = (53.5 - 52.0)/(53.5 - 50.9) = 0.57_7$ .

(Note that since the Q test involves comparison of  $Q_{\text{calc}}$  and  $Q_{\text{tab}}$  - i.e., a further calculation - this number should retain a guard digit.)

**Question 3.** After the removal of the outlier, the data of Question 2 yields  $\bar{x} = 51.4$ ,  $s = 0.4$ . The expected result was 50.6. Systematic error is

- (a) present, because  $t_{\text{calc}} > t_{\text{tab}}$**   
 (b) absent, because  $t_{\text{calc}} > t_{\text{tab}}$   
 (c) present, because  $t_{\text{calc}} < t_{\text{tab}}$   
 (d) absent, because  $t_{\text{calc}} < t_{\text{tab}}$   
 (e) impossible to establish without more information

**Solution:**  $t_{\text{calc}} = \sqrt{n}(\bar{x} - \text{ref})/s = \sqrt{6}(51.4 - 50.6)/0.4 = 4.9$ ;  $t_{\text{tab}} = 2.571$ . Since  $t_{\text{calc}} > t_{\text{tab}}$ , a systematic error does exist at this confidence level.

**Question 4.** The data in Question 3 was expected to have a relative standard deviation of 0.6 %. In practice, the data is:

- (a) significantly less precise, since  $F_{\text{tab}} < F_{\text{calc}}$   
 (b) significantly less precise, since  $F_{\text{tab}} > F_{\text{calc}}$   
 (c) not significantly less precise, since  $F_{\text{tab}} < F_{\text{calc}}$   
**(d) not significantly less precise, since  $F_{\text{tab}} > F_{\text{calc}}$**   
 (e) significantly more precise, since  $F_{\text{tab}} < F_{\text{calc}}$

**Solution:** actual  $\text{rsd} = 0.4/51.4 = 0.7_8 \%$ .  $F_{\text{calc}} = (0.7_8/0.6)^2 = 1.7$ ;  $F_{\text{tab}}(5, \infty) = 2.21$ . The difference is not statistically significant.

**Question 5.** Which expression correctly describes the charge balance for a solution of a weak diprotic acid,  $H_2A$ , of initial concentration  $M_{H_2A}$ ?

- (a)  $M_{H_2A} = [H_2A] + [HA^-] + [A^{2-}]$   
 (b)  $M_{H_2A} = [HA^-] + 2[A^{2-}] + [OH^-]$   
 (c)  $[H^+] = [HA^-] + [A^{2-}] + [OH^-]$   
 (d)  $[Na^+] + [H^+] = [OH^-]$   
**(e)  $[H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$**

**Solution:**  $H^+$  is the only positive ion. There are three negative ions:  $HA^-$ ,  $OH^-$  and  $A^{2-}$  (the last of these "counting twice" since it is a 2- ion). Hence the expression in (e).

**Question 6.** An indicator with a  $pK_{a,HIn}$  of 7.00 is used to locate the endpoint of a weak acid-strong base titration. The  $pK_a$  of the acid is 5.72. The endpoint will

- (a) lead the equivalence point by a substantial amount**  
 (b) lead the equivalence point by a negligible amount  
 (c) correspond exactly to the equivalence point  
 (d) lag the equivalence point by a negligible amount  
 (e) lag the equivalence point by a substantial amount

**Solution:** we know the eqpt pH in such a titration occurs at a  $pH > 7$ , so the endpoint must lead the eqpt (i.e., either (a) or (b) must be correct). Before the eqpt, we have a buffer:

$$pH = pK_a + \log \left( \frac{V \text{ base added}}{V \text{ base not added yet}} \right) = pK_a + \log(\text{"ratio"})$$

At  $pH 7.00$ ,  $\log(\text{"ratio"}) = 7.00 - 5.72 = 1.28 \Rightarrow \text{"ratio"} = 19.0$  i.e. the titration is only  $\sim 95\%$  over! This is a substantial error (eg. for a 10.00 mL endpoint, this endpoint would be 0.50 mL early).

**Question 7.** Of the pH values listed below, give the one at which one of the two metals will give a good titration with EDTA, but the other will not titrate at all.

pH	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0
$\alpha_Y$	1.30E-23	1.90E-18	3.30E-14	2.60E-11	3.80E-09	3.70E-07	2.30E-05	5.00E-04
$K_f'_{M1}$	5.18E-10	7.56E-05	1.31E+00	1.04E+03	1.51E+05	1.47E+07	9.16E+08	1.99E+10
$K_f'_{M2}$	6.52E-11	9.52E-06	1.65E-01	1.30E+02	1.90E+04	1.85E+06	1.15E+08	2.51E+09

- (a) 3.0      (b) 4.0      (c) 5.0      (d) 6.0      **(e) there is no such pH**

**Solution:** such a pH would be one at which one  $K_f'$  is  $10^6$  or greater, and the other  $10^3$  or less. There is no such pH - the two  $K_f'$  values are obviously insufficiently different.

**Question 8.** Using the "quick and dirty" formula (*not* the full quadratic expression), the approximate pH of a 0.0331 M solution of a weak acid with  $K_a = 7.65 \times 10^{-4}$  is:

- (a) **2.30**      (b) 3.63      (c) 4.61      (d) 5.07      (e) none of (a), (b), (c) or (d).

**Solution:**  $[H^+] = \sqrt{K_a \cdot M_{HA}} = \sqrt{(0.0331 \times 7.65 \times 10^{-4})} = 5.032 \times 10^{-3} \Rightarrow \text{pH} = 2.30$ . (Note that pH is quoted only to 2 dp even if more are justified on the basis of calculation.)

**Question 9.** (See previous question). The exact pH of this solution, compared to the approximate value found in the previous question, is

- (a) 0.30 lower      (b) 0.13 lower      (c) 0.03 lower      (d) the same      (e) **0.03 higher**

**Solution:** you don't actually have to do any calculation. Note that the assumption implicit in our answer to Question 8 (that  $[H^+] \ll M_{HA}$ ) is invalid; therefore we should be using  $[H^+] = \sqrt{K_a \cdot (M_{HA} - [H^+])}$ . This can only result in a *lower*  $[H^+]$ , and hence a *higher* pH than before. Only (e) can be correct. If you actually use the iterative formula, you will get  $\text{pH} = 2.33$ , but it's not necessary to do so.

**Question 10.** The conditional formation constant,  $K_f'$ , for a metal ion-EDTA complex allows for the fact(s) that

- (a) not all the "free" EDTA is in the  $Y^{4-}$  form.  
 (b) not all the "free" metal ion is necessarily in the  $M^{n+}(\text{aq})$  form.  
 (c) the formation constant for the metal ion-EDTA complex,  $K_f$ , depends upon solution conditions.  
 (d) **both (a) and (b).**  
 (e) both (a) and (c).

**Solution:**  $K_f' = \alpha_Y \cdot \alpha_M \cdot K_f$ . (a) is true (the  $\alpha_Y$  term is variable); (b) is true (so is the  $\alpha_M$  term); (c) is not true ( $K_f$  is a constant). Hence, response (d).

**Question 11.**

(a) Serum containing  $\text{Na}^+$  gave a signal of 4.27 mV in an atomic absorption analysis. When the concentration of the serum was increased by 0.100 M (with no change in volume), the resulting signal was 7.98 mV. Further additions verified that the response was linear. Calculate the original concentration of  $\text{Na}^+$  in the serum.

(b) What is this procedure called?

(c) Under what circumstances is it used?

(d) Name the major (and unverifiable) assumptions made in this procedure.

**Solution:** (a). Call the initial concentration  $x$ .

Then  $x/(0.100 + x) = 4.27/7.98 \Rightarrow 7.98x = 0.427 + 4.27x \Rightarrow 3.71x = 0.427 \Rightarrow x = 0.115$ . Original concentration is 0.115 M.

(b) Standard Additions.

(c) When a calibration curve is to be constructed where significant matrix effects, potentially different from sample to sample, may be present.

(d) That the response *is linear* below the range measured, right back to the origin; that the response curve *has a zero intercept* below the range measured, right back to the origin.

**Question 12.**

A 20.00 mL sample of a 0.0500 M solution of a weak acid HA,  $K_a = 5.62 \times 10^{-5}$ , is titrated with 0.100 M NaOH. Calculate the pH after the addition of (a) 7.00 mL and (b) 14.00 mL of titrant.

Note that only two marks will be awarded for the actual answers.

**Your answer must include the steps in the box at right. Also, if you make any assumptions, state them, and prove that they are valid.**

1. Characterization
2. Titration Reaction
3. Eqpt titrant volume
4. Type of solution

**Solution:**

1. Weak acid - strong base titration.

2.  $\text{HA(aq)} + \text{OH}^{\text{-(aq)}} \Rightarrow \text{A}^{\text{-(aq)}} + \text{H}_2\text{O(l)}$

3.  $c_1V_1 = c_2V_2 \Rightarrow V_2 = (c_1/c_2)V_1 = (0.0500/0.100) \times 20.00 = 10.0_0 \text{ mL}$ .

4 (a) before eqpt, so this is a buffer; (b) after eqpt, so this is a strong base (excess NaOH).

Now we can start the pH calculations:

(a)  $\text{pK}_a = -\log(5.62 \times 10^{-5}) = 4.25_0$ .

$\text{pH} = \text{pK}_a + \log((V \text{ base added})/(V \text{ base not added yet})) = 4.25_0 + \log(7.00/(10.0_0 - 7.00)) = 4.62$ .

**Assumptions:** that both  $[\text{H}^+]$  and  $[\text{OH}^-]$  are  $\ll$  both  $[\text{HA}]$  and  $[\text{A}^-]$ . True by inspection for  $[\text{OH}^-]$  (which is  $< 10^{-9} \text{ M}$ ).  $3.0_0/10.00$  of the original HA is still present; the volume of the solution has increased from 20.00 mL to 27.00 mL  $\Rightarrow [\text{HA}] = 0.0500 \text{ M} \times 0.30_0 \times (20.00/27.00) = 0.011_1 \text{ M}$ . Since  $[\text{H}^+] = \sim 2.4 \times 10^{-5} \text{ M}$ , the assumption that  $[\text{H}^+] \ll [\text{HA}]$  is valid. Since  $[\text{A}^-] > [\text{HA}]$ , the assumption that  $[\text{H}^+] \ll [\text{A}^-]$  must also be valid.

(b) 4.00 mL of excess strong base have been added; total volume is now 34.00 mL.

Thus,  $[\text{OH}^-] = 0.100 \text{ M} \times (4.00/34.00) = 0.0117_6 \text{ M} \Rightarrow \text{pOH} = 1.92_9 \Rightarrow \text{pH} = 12.07$ .

**Assumptions:** that autolysis is negligible (obviously true;  $[\text{H}^+]$ , which also equals the  $[\text{OH}^-]$  from autolysis,  $\sim 10^{-12}$ ). That the hydrolysis of  $\text{A}^-$  is negligible. There are several ways to prove this; easiest is to calculate  $\alpha_{\text{HA}} = [\text{H}^+]/([\text{H}^+] + K_a) = \sim 10^{-12}/(10^{-12} + \sim 5 \times 10^{-5}) = \sim 2 \times 10^{-6}$ . Only two millionths of the  $\text{A}^-$  (which is now at a concentration of  $\sim 0.0300 \text{ M}$ ) has resulted in  $\text{OH}^-$  production. The total  $\text{OH}^-$  concentration, however, is above  $10^{-2} \text{ M}$ .

(Did you notice that  $\sim$  half the solution involves the assumptions?)